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Improvement of interface structure and magnetic properties of Co on Si (100) by surfactant (Sb) mediated growth

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Abstract In this study thin Co films were grown on Si (100): (1) with one monolayer of Sb as surfactant and (2) without any surfactant. The Co film, its interface with the Si substrate and the behavior of the Sb surfactant layer were investigated during the growth by high-resolution Rutherford backscattering. By the use of Sb, the evaporated cobalt grows in a layer-by-layer mode and the mixing of Co and Si at the interface is strongly reduced. During the evaporation of Co, Sb floats on the surface for all Co coverages with some incorporation in the grown Co film only for higher coverages. The improvement of the interface quality is also reflected in the magnetic properties of the Co film.

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1 Introduction

The ferromagnetic-semiconductor heterostructure could pave the way to a new generation of electronics devices, such as spin memories, spin transistors, and spin quantum computers [1, 2]. High spin polarization of Co at room temperature (∼45%) [3] and long spin coherence length in Si (longer than micrometers) [4] make Co and Si attractive candidates for spin-injection experiments [5]. In such a heterostructure of a Co thin film on a Si substrate, any structural disorder at the interface would drastically reduce the spin polarization at the interface and, hence, the spin injection efficiency [5, 6]. As understood from the growth of Co on Si (100) at room temperature, Co atoms diffuse into the Si lattice and occupy tetrahedral interstitial sites in the Si matrix which is the main cause for the weakening of Si–Si bonds [7–9]. These weakened bonds allow Si atoms to diffuse out to the surface and form silicide-like phases which, in turn, cause spin depolarization. The preparation of a sharp Co/Si interface, therefore, is of crucial practical importance and represents a unique challenge in thin film growth technology.

A significant breakthrough in improving such interfaces was achieved by Copel et al. by using surfactants for the cases of hetero- and homoepitaxial growth [10–13]. The surfactant, due to its low surface free energy, floats on the growth front in this way minimizing the total surface free energy of the system and, hence, reducing interdiffusion. Experiments on surfactant-mediated growth of Co on Cu [14], Co on GaAs [15], and Co on Ge [16] show that the surfactant floats on the Co overlayers, reduces interface reactions, improves the crystalline quality of the Co, and drastically reduces the magnetic dead layer at the interface. Up to now there has no such attempt been made for the surfactant-mediated growth of Co thin films on Si. The lower surface free energy of Sb in comparison to Co and Si makes it a potential candidate for such a task.

In this paper, we present a study of the Sb-mediated growth of Co on Si (100) in an in situ experiment where the quality of the interface, the Co film, and the Sb layer were analyzed during the growth by high-resolution Rutherford backscattering spectrometry (HRBS). In this experiment we have studied the growth of Co on Si with and without Sb as surfactant. We have addressed the following issues which are important for the growth of Co on Si (100) with Sb as surfactant:

1. Does Sb behave as a surfactant for the Si-Co heterostructure and reduce Co-Si interface reactions?

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2. Is there any incorporation of Sb in the growing Co thin film?
3. In addition to these analytical experiments magnetic measurements on the grown Co films were performed in order to correlate interface structure and magnetic properties.

2 Experiment

The sample preparation, i.e., the cleaning of the Si (100) surface, the evaporation of the Co and Sb thin films and the in situ analysis by HRBS were carried out in an ultrahigh-vacuum (UHV) system consisting of a preparation chamber, connected to a Pelletron accelerator and equipped with an electrostatic spectrometer for energy analysis of scattered MeV ions with high energy resolution [17]. Two separate experiments were performed in these investigations: the growth of Co on a clean Si (100) surface (1) without and (2) with Sb as surfactant. For this purpose n-type Si (100) of size 2×2 cm^2 and resistivity 5–10 Ω cm was Shiraki [18] cleaned and immediately transferred into the UHV chamber. The samples were degassed over night and annealed at 750°C for 2 h. Then the samples were heated to 900°C for 30 min and flash heated to 1050°C for several short periods of time to achieve a clean, oxide-free surface. From these high temperatures the samples were slowly cooled down to room temperature. The surface cleanness of the samples was verified by HRBS measurements.

Co with high purity ($4N$) was evaporated from a high-temperature effusion cell on to the clean Si (100) surface which was kept at room temperature. The evaporation rate was about 0.5 ML/min (1 ML $= 6.87 \times 10^{14}$ atoms/cm^2). For the Sb-mediated growth of Co on Si (100), about 1 monolayer of Sb with 3N purity was sublimated from a low-temperature effusion cell on to the clean Si (100) surface at the rate of 0.1 ML/min, followed by Co evaporation. The deposition rates were measured by a quartz microbalance and calibrated by HRBS with an accuracy of about 5%. HRBS measurements were carried out at the Sb, Co and Si high-energy edges of the backscattering spectra for different stages of Co evaporation. All the measurements were performed using 2 MeV He^+ ions at incidence angles of 4.5° for the growth of Co on Si and 7.5° for the Sb-mediated growth, and a scattering angle of 37.5°. For all coverages, the HRBS spectra were taken on new spots (size ∼1 mm^2) within the uniform evaporation region to minimize potential effects of radiation damage by the incident He^+ ions (the effects are small: the repetition of a measurement at the same spot showed deviations which only were of the size of the statistical errors).

The magnetic measurements of very thin Co films on Si (100) with Sb and without Sb as surfactant were performed with a Quantum design SQUID magnetometer. For these SQUID measurements separate HRBS-controlled-growth samples were used. For this purpose a shadow mask was used during the evaporation of Sb, resulting in one half of the sample covered by Sb and the other remaining uncovered. Subsequently a thin film of Co (about 15 ML) was deposited on the sample without mask. Before the magnetic measurements the sample was cut into two halves according to the Sb coverage.

3 Results and discussion

In the first set of experiments Co (2–23.42 ML) was evaporated on Si (100) at room temperature without Sb as surfactant and HRBS spectra were taken at different stages of Co deposition. The evolution of the Co and Si backscattering spectra with increasing coverage is shown in Fig. 1. The HRBS spectra reflect the composition and depth structure of the samples. The part of the spectra in the energy range 1910 to 1935 keV arises from backscattering by the grown Co film, the other part between 1850 to 1885 keV from backscattering by the Si substrate. The spectra, in particular the steps at the Si high-energy edge and the small height of the Co spectra (2–16 ML of Co evaporation) give clear evidence for the formation of Co silicide (the backscattering yield of a pure Co film should be about 2.2 times the yield of the Si); the formation of a pure Co layer seems to start at about 16 ML. Furthermore, up to 16 ML of evaporated Co, the high-energy part of the Si spectrum does not shift from its initial position. This means that Si is present at the sample surface at all stages of Co evaporation up to a coverage of 16 ML. Only for the highest amount of evaporated Co (23.42 ML) an additional peak shoots up in the Co spectrum

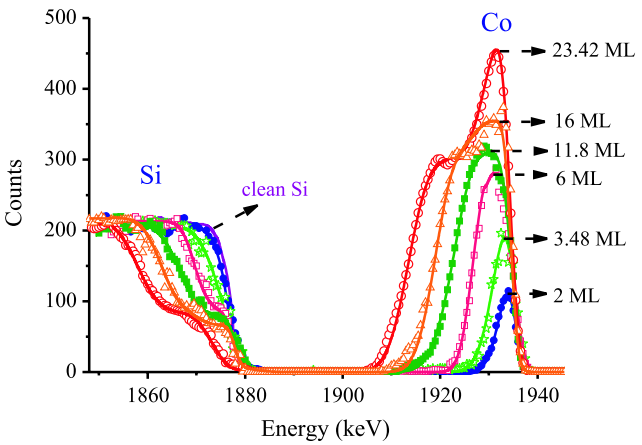

Fig. 1 Backscattering spectra (*symbols*) and RUMP simulations (*solid lines*) for Co deposited on Si (100) (Co coverage from 2–23.42 ML) at room temperature without surfactant. The Co parts and the near-surface Si parts are shown. Only after the deposition of 16 ML of Co a metallic Co film starts to grow

besides a shift of the high-energy edge in the Si spectrum. This shift gives clear evidence that now pure metallic Co starts to grow on top of the silicide phases at the interface.

In order to obtain more detailed information about the depth distributions of Co and Si in these films, the Co spectra were simulated by the program "RUMP" [19]. In these simulations, individual atomic layers (1 ML = 6.87 × 10^{14} atoms/cm^2 = density of Si atoms in (100) Si planes) were considered where each layer was allowed to have its individual composition of Co and Si. The results of these simulations are included in Fig. 1 by solid lines through the data points. The elemental distributions of Si and Co as obtained from these simulations are shown in Fig. 3a. As the figure shows, for 2 ML of evaporated Co, a Co-silicide phase with composition close to CoSi ($Co_{0.6}Si_{0.4}$) is formed at the surface (it should be noted that this deviation from the stoichiometric composition $Co_{0.5}Si_{0.5}$ is clearly evidenced by the data: a fit with the trial concentration $Co_{0.5}Si_{0.5}$ would not match the experimental data). This composition stays the same with increasing amount of Co up to an amount of about 6 ML, with only the silicide film getting thicker. Between 6 ML and 11.83 ML, the composition changes into stoichiometric CoSi at the surface, followed by a $CoSi_2$-like phase at the interface. This interface structure seems to remain stable up to larger amounts of evaporated Co. At about 16 ML of Co, a Co_2Si phase appears at the surface, in addition, with the interface structure itself unchanged. No metallic Co is formed up to this coverage. Finally, for 23.42 ML of evaporated Co, the interface structure is still unchanged, only the CoSi layer now being thicker. But now 7 ML of pure metallic Co show up at the very surface (followed by 4 ML of Co_2Si, 25 ML of CoSi, and 4 ML of $CoSi_2$). The total amount of Co atoms in these silicide phases is 16.5 ML. This means that metallic Co starts to grow only after the deposition of about 16.5 ML of Co. In Fig. 3b the evolution of the CoSi-like phase with the Co deposition is illustrated. It shows that the fraction of Co in the CoSi-like phase remains high ($Co_{0.6}Si_{0.4}$) right from the beginning and approaches the stoichiometric CoSi value for higher coverages. The thickness of the CoSi-like layers increases initially rapidly with the amount of deposited Co, reaches then a plateau (for coverages of 11.83 and 16 ML; the rest of the Co atoms form different types of silicides) and again increases for higher coverages.

A substantial modification of the growth mode is obtained by introducing Sb as a surfactant. For this purpose ∼1 ML of Sb was evaporated on a clean Si (100) surface. Subsequently Co films of increasing thicknesses were deposited on this substrate and the sample was analyzed by HRBS at the different stages of Co deposition. The HRBS spectra are shown in Fig. 2 together with RUMP simulations of the spectra. The figure also includes the spectra of the Si surface before and after Sb deposition. As shown in the figure, the Sb and Si spectra of the Si sample with ∼1 ML Sb

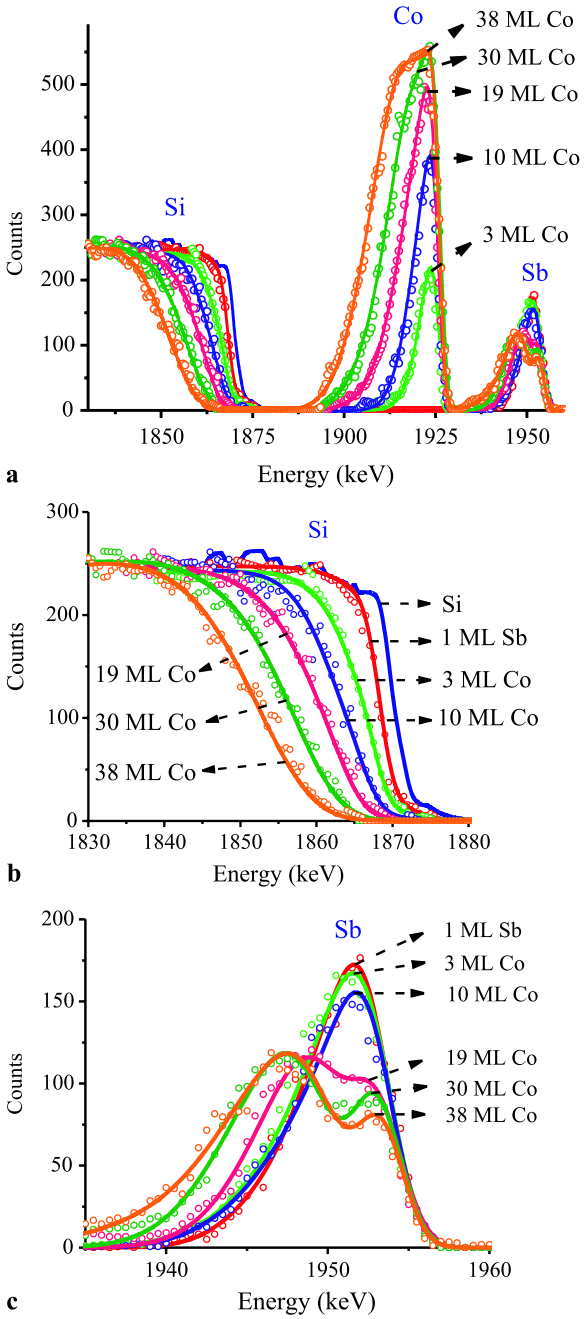

Fig. 2 Rutherford backscattering spectra (*symbols*) and RUMP simulations (*solid lines*) for Sb-mediated growth of Co on Si (100) (**a**) overview about the HRBS spectra during the deposition of Co (3–38 ML) on Si (100). A metallic Co film starts to grow almost from the beginning of Co deposition. (**b**) Shift of the high-energy Si edge due to Sb and subsequent Co deposition. (**c**) Change of the Sb spectra with increasing Co coverage

can be simulated with RUMP under the simple assumption of one continuous monolayer of Sb (0.687 × 10^{14} at/cm^2) with slight roughness (thickness fluctuations of 0.5 ML). This roughness is most likely a natural consequence of the large (16%) difference between the covalent radii of Sb and Si [20]. The complete coverage of the Si surface by the Sb

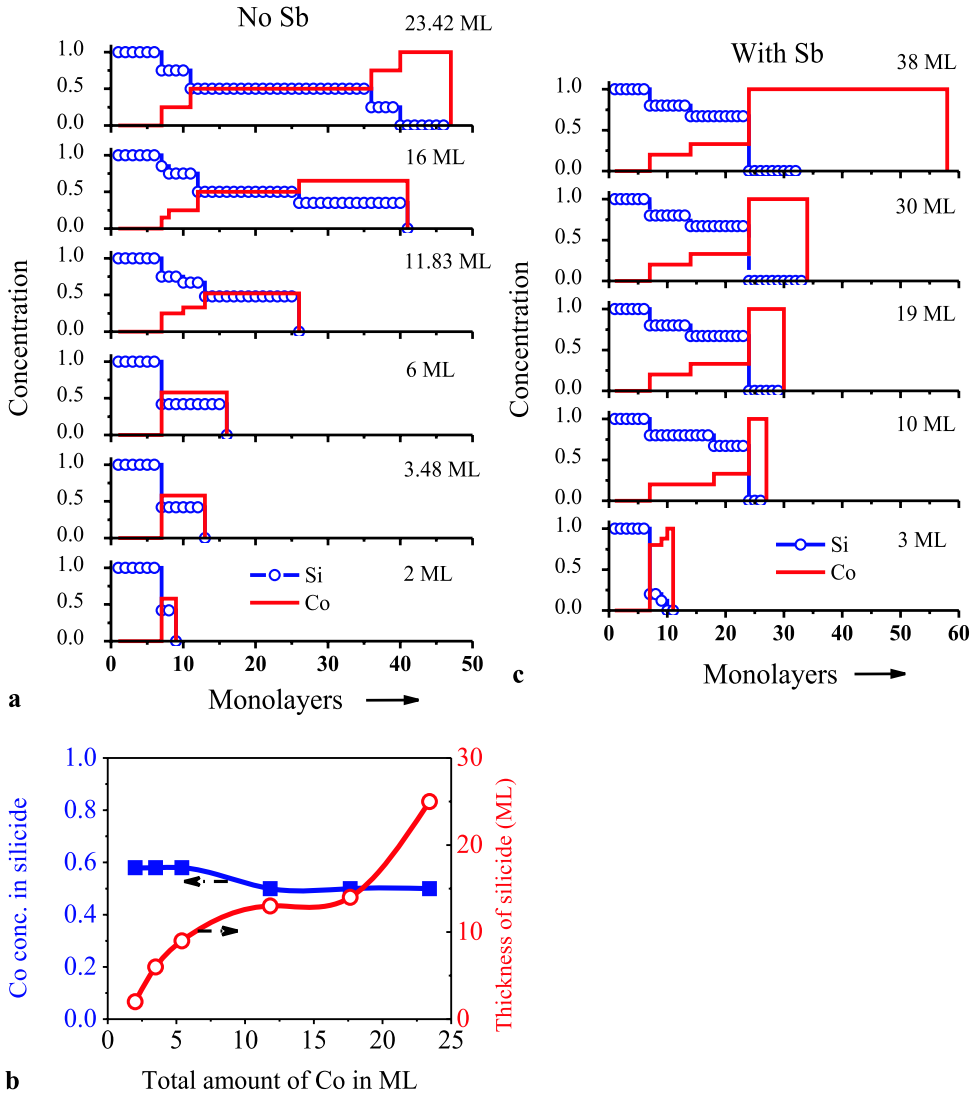

Fig. 3 (**a**) Elemental distributions of Si and Co for the growth of Co (2–23.42 ML) on Si (100) without Sb as surfactant. (**b**) Co content (Co/Co+Si) in the CoSi-like interface layer (*left scale*) and thickness of CoSi-like layer (*right scale*) of the samples of (**a**) versus the amount of evaporated Co. (**c**) Elemental distributions of Si and Co for the growth of Co (3–38 ML) on Si (100) with Sb as surfactant

layer is also clearly evident from the almost parallel-shift of the Si high-energy edge position from 1870 to 1868.2 keV (energies at half height) after the Sb evaporation (Fig. 2b).

Figure 2 also shows Rutherford backscattering spectra and RUMP simulations of the elements Si and Co. For 3 ML of Co, the simple parallel shift of the Si high-energy edge position gives clear indication for the growth of metallic Co on the Si surface; no Si is found at the sample surface. Also from the RUMP simulation (Fig. 3c) we find that metallic Co grows on the surface with 1 ML of a $CoSi_2$-like phase at the interface. From looking at the (almost parallel) shift in the Si high-energy edge position in Fig. 2b for all coverages (3–38 ML) it is clear that a layer-by-layer growth of Co occurs. The absence of any step-like structures in the Si spectra (as seen in Fig. 1), in addition gives evidence that a much sharper interface has formed in the case of Sb-mediated growth. The concentration profiles of Si and Co as obtained from the RUMP simulations are shown in Fig. 3c. From this figure it is evident that the growth of a pure metallic layer starts from the very beginning of the evaporation (3 ML of Co); its thickness increases with increasing coverage. After 19 ML of deposited Co, a well-defined interface structure has established which consists of about 10 ML of $CoSi_2$ and 7 ML of $CoSi_4$ (low-Co-content silicide) and persists more or less unchanged up to higher coverage. The total amount of Co in these silicide phases has been drastically reduced to 4.7 ML only (and is much smaller than the amount of 16.5 ML in interfaces grown without surfactant mediation). This thin and low-Co-content silicide phases do not give rise to any step in the Co and Si HRBS spectra, but give rise to tails at the low-energy side of the Co spectra (see Fig. 2a) and to a slight nonparallel shift of the high-energy edge of the Si spectra (see Fig. 2b). We want to note that this amount of 4.7 ML of Co in silicide phases at the interface is also lower than the amount of Co in silicide phases (4.93 ML) when Co is deposited on Si at −60°C [21].

When summarizing the results of the last paragraphs one can state: (1) Without Sb as surfactant, metallic Co starts to grow only after the deposition of about 16.5 ML of Co, while with Sb it grows almost from the beginning. (2) Without Sb as surfactant an about stoichiometric CoSi phase is formed at the interface which grows to a (in the present experiment) maximum thickness of 25 ML, besides thinner transition layers at the surface and the Si side (8 ML). (3) With the use of 1 ML of Sb as surfactant, metallic Co grows at the surface almost from the beginning of evaporation and (4) explicitly low-Co-content silicide interfaces are formed which remain almost unchanged starting at a deposition of 10 ML of Co. This clearly indicates that Sb successfully prevents the out-diffusion of Si through the growing Co film due to its low surface energy, but can not prevent the in-diffusion of Co into the Si bulk completely. In this way it can however reduce the formation of high-Co-concentration silicides.

A strong tendency for surface segregation is an important condition for the effectiveness of Sb as a surfactant. If we look at the Sb backscattering spectra for all Co coverages (Fig. 2c), we see that the Sb high energy edge remains at the same energy position even after 38 ML of Co deposition. This indicates that the Sb floats on the Co surface, obeying its surfactant behavior. For the 3 and 10 ML case there is no change of the shape of the Sb spectrum except a slight decrease in the height of the Sb peak. This reduction can be attributed to the surface roughness after Co evaporation. For the cases of 19, 30, and 38 ML the spectra change drastically, showing some incorporation of Sb in the grown Co film—besides Sb at the surface. In fact, the bulk solubility limit of Sb in Co is well below 1% at room temperature [22]. This incorporation of Sb may therefore be due to the relatively low growth temperature (room temperature) employed in this experiment and the increasingly roughening of Co the film: Sb atoms in holes are just covered by the arriving Co atoms.

As seen in these experiments, metallic Co starts to grow only after about 16.5 ML of evaporated Co if no Sb is used, while with the use of Sb, metallic Co starts to grow almost from the beginning. This difference should, naturally, also show up in the magnetic properties of these films. In order to study the magnetic properties, ∼15 ML of Co were evaporated on Si (100) (1) with and (2) without Sb as surfactant by use of a shadow mask as described at the end of Sect. 2. The magnetization curves of these two types of samples as measured at 300 K with the SQUID magnetometer are shown in Fig. 4. They exhibit some important features which are discussed here. (1) Both samples are ferromagnetic at room temperature. This means that the sample grown without Sb (where all Co atoms are in silicide-like phases) is magnetic even at room temperature. (2) The sample grown with Sb as surfactant shows a higher saturation magnetization than the sample grown without Sb. The reason apparently lies

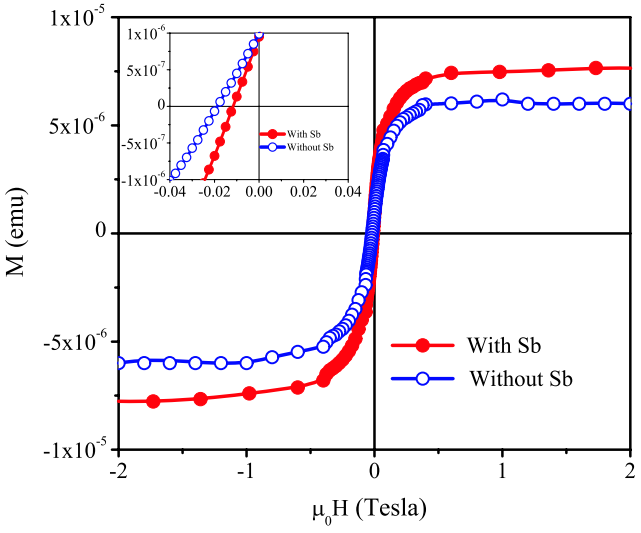

Fig. 4 Magnetization curves of ultra-thin (∼15 ML) Co films on Si (100) deposited with and without Sb at room temperature. The *inset* shows the magnified version of the magnetization curves around the origin showing clear remanence and coercive fields

in the improved interface quality of the surfactant-mediated grown sample: a larger amount of metallic Co and a lower Co-concentration of the silicide phases (samples exhibiting higher amounts of metallic phase commonly yield higher saturation magnetization). The increase of the saturation magnetization (and of the magnetic moment per Co atom) is found to be 20% (we want to note that the total amounts of Co in these two samples were controlled by HRBS measurements during evaporation and are identical within an accuracy of about 5%). (3) The sample grown with Sb shows a coercive field of 0.0117 T which is lower than that of the sample grown without Sb (0.0187 T). The silicide layers of the latter sample apparently act as magnetic pinning layers and in this way provide the increased coercive field.

4 Summary

The present paper has shown that in MBE growth of Co on Si (100) without Sb as surfactant, metallic Co starts to grow only after the deposition of about 16.5 ML of Co. At the interface 33 ML of various silicide phases are formed (25 ML of stoichiometric CoSi phase, besides 8 ML of transition layers at the surface and the Si side). By the use of Sb as surfactant the metallic Co starts to grow almost from the beginning in a type of layer-by-layer mode. However, also low Co-content silicide phases are formed with a total thickness of about 17 ML which after an initial phase remain independent of the amount of deposited Co. The total amount of Co in these silicide phases is only about 4.7 ML, which is significantly less than the amount of 16.5 ML obtained without surfactant. This drastic reduction of the silicide thickness

and the observation of low Co content silicides only, give clear evidence that the out-diffusion of Si has been reduced by the presence of the surfactant. The Sb is found to float on the surface of the Co film for all the Co coverages except for a small amount of Sb incorporated in the grown Co film at higher coverage. The improved interface quality with Sb-mediated growth can also be seen in the magnetic properties of the evaporated film: Sb-mediated grown Co shows a higher saturation magnetization and a lower coercive field.

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